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STUDIES INVOLVING SINGLE HYDROGEN-BRIDGE BORANES

DISSERTATION

Presented in Partial Fulfillment of the Requirements for the Degree Doctor of Philosophy in the Graduate School of The Ohio State University

By
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* * * * * *

The Ohio State University
1969

Approved by
Adviser
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Professor Sheldon G. Shore
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I. INTRODUCTION

A. Background

1. Diborane (6) reactions with Lewis bases

The reaction of diborane (6) with Lewis bases has been the topic of extensive study in recent years. The cleavage of the hydrogen bridge system into products which contain BH$_3$ groups is commonly called "symmetrical cleavage". The reaction is represented by the following scheme where L represents the Lewis base:

\[
\begin{align*}
\text{H} & \quad \text{B} & \quad \text{H} & \quad \text{B} & \quad \text{H} \\
\text{H} & \quad \text{B} & \quad \text{H} & \quad \text{B} & \quad \text{H} \\
\end{align*}
\]

\[+ 2L \rightarrow 2LBH_3\]

The cleavage reaction involves the rupture of electron deficient bridge bonds, which have a significant energy of formation. Modern values for dimerization of borane, 2BH$_3$=B$_2$H$_6$, have been reported to be approximately -36 to -38 kcal/mole (1,2,3). Typical Lewis bases which cleave the diborane (6) molecule symmetrically are (CH$_3$)$_3$N (4), CO (5), tetrahydrofuran (6), (CH$_3$)$_2$PH (7), (CH$_3$)$_3$P (8), and (CH$_3$)$_2$S (9).

Diborane (6) is capable of reacting with other electron pair donors to produce ionic products, BH$_2$L$_2$ BH$_4$.
In cases where ionic products are generated, the reaction is termed an "unsymmetrical cleavage" reaction and is represented by the following equation:

\[ \text{H}_3\text{B(NH}_3\text{)}_2 \text{BH}_4 \text{ only detectable product} \]

\[ \text{H}_2\text{B(NH}_2\text{CH}_3\text{)}_2 \text{BH}_4 \rightarrow \text{H}_3\text{BNH}_2\text{CH}_3 \]

\[ \text{H}_3\text{BNH(CH}_3\text{)}_2 \rightarrow \text{H}_2\text{B[NH(CH}_3\text{)}_2\text{]}_2 \text{BH}_4 \]

The controlled addition of diborane (6) to ammonia leads to apparent unsymmetrical cleavage of the hydrogen-bridged bonds, resulting in the formation of the "diammoniate of diborane", \([\text{bis(diamine)dihydroboron(1+)}\text{hydroborate}] (5,8,10,11,12,13,14,15,16,17,18)\). Direct reaction of diborane(6) with \(\text{NH}_2\text{CH}_3\) and \(\text{NH(CH}_3\text{)}_2\) has been shown to produce symmetrical and unsymmetrical cleavage products (19), while earlier literature suggested that simple borane adducts are formed in these reactions (20,21,22).

The factors determining the type of cleavage product are several and undoubtedly complicated. One major factor is obviously a steric requirement, considering the change in the type of cleavage observed with progressive methyl substitution on nitrogen in going from ammonia to \(\text{N(CH}_3\text{)}_3\). The reactions of diborane (6) with \(\text{NH}_3\), \(\text{NH}_2\text{CH}_3\), \(\text{NH(CH}_3\text{)}_2\), and \(\text{N(CH}_3\text{)}_3\) were found to be the following (4,15,19):

\[ \text{H}_2\text{B(NH}_3\text{)}_2 \text{BH}_4 \text{ only detectable product} \]

\[ \text{H}_2\text{B(NH}_2\text{CH}_3\text{)}_2 \text{BH}_4 \rightarrow \text{H}_3\text{BNH}_2\text{CH}_3 \]

\[ \text{H}_3\text{BNH(CH}_3\text{)}_2 \rightarrow \text{H}_2\text{B[NH(CH}_3\text{)}_2\text{]}_2 \text{BH}_4 \]
In addition to the amine bases cited above, dimethyl sulfoxide is the only other well-documented example of unsymmetrical cleavage of diborane (6) (23).

The most useful analytical method for distinguishing the type of cleavage products generated in the reaction of diborane (6) and Lewis bases has been boron-11 nuclear magnetic resonance spectroscopy. A boron-11 nucleus which has three hydrogen atoms bonded to it, as in H₃BN(CH₃)₃, will give a quartet in the boron-11 nuclear magnetic resonance spectrum due to spin coupling of the hydrogen atoms with the boron nucleus. The spectrum would be further complicated if the Lewis base bonded to boron in the symmetrical product, also spin coupled with the boron nucleus. In the cases where the unsymmetrical cleavage products are generated, the boron nuclei are readily distinguished by their multiplicity in the boron-11 nmr spectra: a quintet due to BH₄⁻ and triplet arising from BH₂L₂⁺. This method has been shown to be very effective (19,23).

Since the hydrogen bridge system of diborane (6) can undergo two apparently different types of cleavage reactions, it has been postulated that diborane (6) reacts in a stepwise fashion (15). The first step involves the displacement of one hydrogen bridge position.
The second step, involving displacement of the remaining bridge hydrogen, determines the type of product.

\[
\begin{align*}
L^B - H - BH + L & \longrightarrow LUBL^B BH, \quad \text{unsymmetrical cleavage} \\
L^B - H - BH + L & \longrightarrow 2LBH_3, \quad \text{symmetrical cleavage}
\end{align*}
\]

Such a scheme is consistent with the observation, made earlier, that with increasing methyl substitution on nitrogen in going from ammonia to \(N(CH_3)_3\), the yield of symmetrical cleavage product increases (4,15,19).

There have been no reported cases where the proposed intermediate in the stepwise cleavage has been isolated and characterized. However, diborane (6) and ammonia have been studied calorimetrically (24) and cryoscopically (17) indicating an intermediate. In several related systems (13,14, 15,16,26,27,28,29,30) there exists evidence for analogous intermediates.

It has been suggested that reactions of diborane (6) with Lewis bases at low temperatures can involve unsymmetrical cleavage, but that the product can readily rearrange to a symmetrical cleavage product, depending upon which form is more stable, thermodynamically, at a particular temperature.
There is no evidence for facile rearrangement in amine diborane (6) systems. Thus, $H_3NBH_3$ and $H_2B(NH_3)^{+}BH_4^-$ shows no tendency toward interconversion in liquid ammonia (13,14,15,16).

2. 1,2-Bis(tetramethylene)diborane (6) reaction studies

The reaction of butadiene and diborane (6) has been reported (31) to give the product 1,2-tetramethylene-2,2-tetramethylenediborane (6) as shown in structure (I).

(I)

The properties exhibited by the organodiborane were unusual with respect to those observed in other tetraorganodiboranes. Brown reported that butadiene and diborane (6) react at room temperature to form a polymeric organoborane (32). The properties of the polymer differ from those observed by the earlier workers. It was suggested that 1,1-tetramethylene-2,2-tetramethylenediborane (6) has properties which are more consistent with an isomeric structure containing a transannular boron hydrogen bridge system, 1,2-bis(tetramethylene)diborane (6) (II).
The resolution of this problem was the major point of a recent study (33). The isolation of (II) was accomplished by four different methods. By comparing the published spectrum of (I) to the solution spectrum of 1,2-bis(tetramethylene)-diborane (6), it was shown that the compounds were identical.

The major piece of evidence toward the elucidation of the structure of (II) came from molecular weight studies. If one considers the symmetrical cleavage products of the molecule in question, with Lewis bases, it is obvious that the calculated molecular weights will be twice as great for 1,2-bis(tetramethylene)-diborane (6) as in the case of 1,1-tetramethylene-2,2-tetramethylenediborane (6).
The experimental molecular weight data obtained (33) can only be interpreted to mean that the parent organodiborane reactant was 1,2-bis(tetramethylene)-diborane (6).

The reaction of 1,2-bis(tetramethylene)-diborane (6) has been reported with ammonia and the methyl-substituted amines (33). It was found that $\text{N(CH}_3\text{)}_3$, $\text{NH(CH}_3\text{)}_2$ and $\text{NH}_2\text{CH}_3$ cleaved the organodiborane symmetrically. Ammonia was the only reactant to produce unsymmetrical cleavage.

The products were identified by their boron-11 nmr spectra. The symmetrical products consisted of a doublet due to hydrogen spin coupling with boron. The spectrum of the unsymmetrical cleavage product of the reaction with ammonia showed both the triplet of the anionic boron and the sing-
let of the cationic boron.

The results of the reaction of 1,2-bis(tetramethylene) diborane (6) with Lewis bases when compared with the analogous reactions with diborane (6) allow for some observations concerning the factors involved when a Lewis base reacts with a hydrogen-bridge system.

Although factors which determine whether a Lewis base will produce symmetrical or unsymmetrical cleavage are still not understood, steric factors certainly play an important role. The tendency to cleave the hydrogen-bridge system unsymmetrically in the diborane (6) compounds reported, diminishes with increased alkyl substitution on both the amine and the diborane (6). Young and Shore (33) also found 1,2-tetramethylenediborane (6) to fit in between diborane (6) and 1,2-bis(tetramethylene)diborane (6) in its reactions with Lewis bases. Thus, in the reaction of diborane (6) with N(CH₃)₃, the symmetrical product alone is found; a less hindered base NH(CH₃)₂ cleaves 1,2-tetramethylenediborane (6) symmetrically; and an even less hindered base NH₂CH₃ cleaves the bridge hydrogen system of 1,2-bis-(tetramethylene)diborane (6) symmetrically. The types of cleavage produced and the relative yields for the diborane (6) and organodiborane reactions with amine bases are presented in Table 1.
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<th>NH$_3$</th>
<th>NH$_2$CH$_3$</th>
<th>NH(CH$_3$)$_2$</th>
<th>N(CH$_3$)$_3$</th>
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<td>B$_2$H$_6$</td>
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<td>Unsymmetrical</td>
<td>Symmetrical only</td>
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B. Statement of Problem

The reaction of diborane (6) with Lewis bases has been postulated to be a stepwise reaction (15). The existence of an intermediate resulting from attack of the base on the diborane (6) molecule has been suggested by several workers (17,24,29).

\[
\begin{align*}
\text{H}_2\text{B} & \quad \text{H} \\
\text{H} & \quad \text{H} \\
\end{align*}
\]

\[+\text{L} \rightarrow \text{H}_2\text{B}-\text{H-BH}_3\]

\[\text{L}=\text{Lewis base}\]

Related systems which may contain single hydrogen-bridge bonds analogous to the intermediate above have been reported (26,27,28,29,30). Brown and coworkers found that triethylamine borane and pyridine borane added a second borane unit to the Lewis base (30). Since boron-11 nuclear magnetic resonance was not available to Brown, the sole basis for the work was the tensiometric titrations.

Preliminary boron-11 nuclear magnetic resonance data on the intermediates reported by Brown, indicated that these particular systems would not be amenable to study by this technique. The spectra obtained were marked by the broadness of the peaks, apparently due to the high viscosity of monoglyme and diglyme solutions at reduced temperature. When the temperature was increased, the spectra sharpened, but the intermediate had disproportionated into the borane
adduct and diborane (6).

The problem to be considered was to attempt to find a system which would allow for preparation and characterization of the intermediates proposed to be involved in the postulated stepwise reaction of diborane (6) with Lewis bases. The intermediates would be reacted with the appropriate Lewis base to see if the product generated would be the same as that obtained upon reaction of diborane (6) directly with excess of the aforementioned Lewis base. The intermediates would be studied by boron-11 nmr while the final reaction products would be identified by the technique already employed in earlier studies (4,15,19).

After the above work had progressed and yielded some meaningful results, a communication was published (34). Eastham reinterpreted the boron-11 nmr data, concluding that the material studied was effectively an intact diborane (6) molecule with the ligand symmetrically attached through a \( \pi \) bond between a nonbonding orbital of diborane (6) and the lone electron pair of the amine (35).

\[
\begin{align*}
\text{H}_2\text{B} & \quad \text{H} \\
\text{H} & \quad \text{BH}_2 \\
\text{L} & \quad \text{amine}
\end{align*}
\]

Pertinent experiments were devised to determine whether Eastham's intermediate or the intermediate discussed in the stepwise cleavage was most reasonable. A boron-11 tracer study and thermodynamic data spoke against Eastham's inter-
mediate. The results were presented in a second communication (36). Additional studies on the intermediates indicated that there might be some complication in the boron-11 nmr spectrum due to an exchange process.

Since the additional studies intended to be undertaken were contingent on a straightforward and uncomplicated system, it was decided to pursue studies in a closely related area.

The recently reported Lewis base reactions with 1,2-bis(tetramethylene)diborane (6) showed that the organodiborane with its transannular hydrogen-bridge system is similar to diborane (6) in its reactions (33).

Pentaborane has been reacted with alkyl lithium reagents to generate a new boron hydride anion in which it is believed that a bridge hydrogen is removed (37,38).

\[
\text{RLi} + \text{B}_9^5\text{H}_9 \rightarrow \text{R-H} + \text{LiB}_5\text{H}_8
\]

The interest in single hydrogen-bridge systems seemed to be heightened by the possibility that an alkyl lithium might deprotonate a bridge hydrogen from 1,2-bis-(tetramethylene)diborane (6).
The reaction between methyl lithium and the organodiborane was carried out and there was no evidence of any methane evolution. Instead of deprotonating, it appeared that the methyl lithium added to 1,2-bis(tetramethylene)diborane (6) and the boron-11 nuclear magnetic resonance of the resultant product indicated a single hydrogen-bridge system.

$$\text{MeLi} + \text{B}\text{H}_2\text{B}_2\text{H}_2\rightarrow \text{Li}^+\text{H-B-H-B-CH}_3$$

It was decided to study the reaction of the anion with amines, since the CH$_3^-$ anion is electronically analogous to ammonia and hence the system would be analogous to adding a single molecule of ammonia to the organodiborane.

$$\text{NH}_3 + \text{B}\text{H}_2\text{B}_2\text{H}_2\rightarrow \text{H-B-B-NH}_3$$

The boron to which the second amine attaches itself, determines whether a symmetrical or unsymmetrical cleavage product is formed. These results could then be correlated with those obtained from the amine reactions (33) of 1,2-bis(tetramethylene)diborane (6).
II. EXPERIMENTAL

A. Apparatus

1. Vacuum system

All reactants and products were manipulated in a standard vacuum system similar to that described by Sanderson (39) and in a variety of nitrogen atmosphere dry-boxes. The vacuum system consisted of a pumping section, a main manifold, three reaction trains (two of which could be separated into two independent sections by glass vacuum stopcocks and the third was constructed using Fisher and Porter Company Teflon vacuum stopcocks), one five liter storage bulb, and a calibrated Töpler system. Volumes were calibrated with sulfur hexafluoride by standard methods (39).

The pumping system consisted of a high capacity Duo-Seal forepump and a two stage mercury diffusion pump filled with triple distilled mercury. The diffusion pump could be bypassed when necessary, by a two-way stopcock, to avoid contamination of the hot mercury. A liquid nitrogen cold trap preceded the two-way stopcocks.

The reaction trains contained several reaction sections consisting of a standard taper 14/35 inner joint separated from the reaction manifold by a vacuum stopcock. On each station was a mercury blowout between the joint and the
stopcock. All the reaction trains were connected to the main manifold. By these reaction trains, materials were introduced into the vacuum system and reaction vessels were attached.

The distillation train consisted of four individually calibrated traps, each approximately 150 ml in volume and three mercury manometers. Each trap could be isolated individually or used for low temperature fractionation of gaseous mixtures as well as for measurement of condensible gases.

The five liter storage bulb was connected to the distillation train by a vacuum stopcock.

A medium capacity Cenco pump was used to operate the Töpler pump.

2. Handling of reactants

Reactions were generally carried out in glass vessels with standard taper joints which could be separated from the mercury "blowouts" by a vacuum stopcock adapter. Some reactions were carried out under grease-free conditions through the use of Fisher and Porter Company 9 mm joints and Fisher and Porter Company Teflon vacuum stopcocks. Non-volatile materials were introduced into the reaction vessels in the dry nitrogen atmosphere of a dry-box and were subsequently transferred to the vacuum system without exposure to air or moisture.
3. **Infrared spectra**

Infrared spectra were run in the gas phase using a cell with windows of Eastman Kodak's infrared transmitting material, "IRTRAN-4". The cell was equipped with a vacuum stopcock so that it could be sampled on the vacuum line. Liquid and highly solvated solids were studied as thin films on KBr plates. Solid spectra were studied as nujol or hexachlorobutadiene mulls pressed between KBr plates. The instrument used to obtain spectra in the 2.5 to 16 micron region was the Perkin-Elmer 337 recording grating spectrometer. Each spectrum was calibrated by superimposing the spectrum of polystyrene.

4. **Nuclear magnetic resonance spectra**

Boron-11 nuclear magnetic resonance spectra were obtained using Varian HR-60, equipped with a 19.3 MHz oscillator, and HR-100, equipped with a 32.1 MHz oscillator, high resolution spectrometers. Proton spectra were obtained with a Varian A-60 spectrometer equipped with an integrator. Low temperature spectra were obtained using a Varian temperature controller which regulated a stream of cooled nitrogen gas to be passed over the sample tube. Spectra obtained with the HR-60 and HR-100 spectrometers were calibrated by the sideband technique and the use of external references of trimethylborate and boron trifluoride etherate.
5. Mass spectra

Mass spectra were obtained using an Associated Electrical Industries, Ltd., Model MS10 mass spectrometer. Samples were connected to the instrument by means of a 14/35 inner joint attached to the inlet system of the spectrometer. Sample gas was introduced and run at a pressure of $5 \times 10^{-6}$ mm Hg. The masses which could be observed were 2, 3, 12-45 and 36-200.

6. X-ray data

X-ray diffraction powder patterns of crystalline solids were obtained using a Debye-Scherrer camera of 11.46 cm effective diameter and a North American Phillips x-ray generator. The solid was ground to a fine powder and put in a .3 or .5 mm capillary. The capillary was sealed by flame and mounted in the camera. The camera was loaded with film and exposed for 10-24 hours (depending on the compound) using a copper target ($K_\alpha = 1.5418$ Å) with a nickel filter and operating at 32 kilovolts and 12 milliamperes.

7. Töpler system

Gaseous reaction products were first passed through a U-tube trap at liquid nitrogen temperature before entering the Töpler pump. The trap was filled with $\frac{1}{4}$ inch glass helices for greater cold surfaces. The Töpler pump was an Eck and Krebs type 4100. The gasometer system, equipped
with an auxiliary demountable bulb to give greater volume,
had been calibrated with sulfur hexafluoride following stand-
ard procedures (39).

8. **Glassware**

All glassware, prior to use, was washed in alcoholic
potassium hydroxide, rinsed with acetone, placed in an oven
at 125° for several hours, and then taken to the vacuum line
or to the dry-box while still above room temperature.

9. **Reaction vessels incorporating nuclear magnetic resonance sample tubes**

Three different types of apparatus were used to prepare 5 and 15 mm nmr sample tubes. In the case of the 5 mm sample tubes, the volatile reactants were distilled while the non-volatile reactants were introduced in the dry-box. The vessels were equipped with 5 mm nmr sidearm tubes, into which the reaction mixtures could be poured following reaction. When a grease-free system was required, the Fisher and Porter Company Teflon vacuum stopcocks and 9 mm glass joints were used. When possible, the volatile reactants were distilled directly into the sample tube fitted with a Fisher and Porter Company Teflon vacuum stopcock and allowed to react at the desired temperature.

In the case of the 15 mm sample tubes, the volatile reactant were distilled directly, while the non-volatile
reactants were introduced in the dry-box and allowed to react.

10. Handling of 1,2-bis(tetramethylene)diborane (6)

1,2-Bis(tetramethylene)diborane (6) has a vapor pressure of approximately 1 mm at 25°; it is a mobile liquid. However, it has a high affinity for stopcock greases and procedures were devised to handle the substance in a grease-free system. The reservoir, shown in Figure 1, was constructed. It was attached to the apparatus used in the preparation of 1,2-bis(tetramethylene)diborane (6). The product, to be stored, was pumped into the U-portion of the reservoir. When 1,2-bis(tetramethylene)diborane (6) was needed, a reaction vessel was attached to the reservoir and the liquid was condensed into the vessel. The reaction vessel and the reservoir were constructed using Fisher and Porter Company 9 mm joints with a Teflon sleeve.

B. Starting Materials

1. Diborane (6)

Diborane (6) was obtained from Callery Chemical Company. It was stored at liquid nitrogen temperature in the sidearm of a five liter storage bulb. When needed, the diborane (6) was transferred to the distillation train by removing the liquid nitrogen from the sidearm. Measurement was made as a gas at room temperature. Periodically, low
Figure 1. Reservoir for storage of 1,2-bis(tetramethylene)-diborane.
temperature fractional distillation was used to check purity.

2. $^{10}$-diborane (6)

$^{10}$-diborane (6) was prepared from $^{10}\text{F}_3\cdot\text{Et}_2\text{O}$ by reacting it with LiAlH$_4$ in diethyl ether (40). CaF$_2\cdot^{10}\text{F}_3$ (95% $^{10}$) was obtained from Oak Ridge National Laboratory and heated to 180° to free the $^{10}\text{F}_3$. Diethyl ether was used to form the complex and for the reaction solvent. LiAlH$_4$ was added and the $^{10}$-diborane (6) that was produced was fractionated at low temperature to separate it from diethyl ether. It was identified by its infrared spectrum, mass spectrum, and vapor density.

3. Deuterodiborane (6)

Deuterodiborane (6) was prepared from LiAlD$_4$ (99-atom % STOHLER ISOTOPE CHEMICALS) and $^{3}\text{B}\cdot\text{OEt}_2$ in the same way as 2. It was identified by its infrared spectrum, mass spectrum, and vapor density.

4. 1,3-Butadiene

Reagent grade 1,3-butadiene was obtained from the Matheson Company. It was purified by low temperature fractional distillation and stored at -196° in the vacuum system. Measurement was made as a gas at room temperature.
5. **Trimethylamine**

Reagent grade trimethylamine was obtained from the Matheson Company and stored at room temperature over P₂O₅ to remove, by reaction with P₂O₅, dimethylamine which was found to be present in the trimethylamine. The material was measured as a gas at room temperature.

6. **Dimethylamine**

Anhydrous dimethylamine was obtained from the Matheson Company. It was taken from the cylinder into the vacuum system where it was measured as a gas at room temperature.

7. **Methylamine**

Anhydrous methylamine was obtained from the Matheson Company. It was taken from the cylinder and measured in the distillation train at room temperature and condensed into the reaction vessel.

8. **Ammonia**

Anhydrous ammonia was obtained from the Matheson Company and used directly from the cylinder. In some cases, it was checked for purity by its infrared spectrum.

9. **Trimethylamine borane**

Trimethylamine and diborane (6) were reacted in a
2:1 ratio at -78° in dichloromethane. The solvent was removed at -45° and the crystalline trimethylamine borane was identified by its melting point, infrared spectrum and boron-11 nmr spectrum. It was placed in a reaction vessel and weighed by difference or prepared in the reaction vessel.

10. Methyamine borane
11. Ammonia borane

Methyamine borane and ammonia borane were prepared according to the following reactions described by Geanangel and Shore (41).

\[ \text{O·BH}_3 + \text{amine} \rightarrow \text{amine·BH}_3 + \text{O·BH}_3 \]

The purified products were checked by their boron-11 nmr spectra, x-ray powder patterns and mass spectra. The boranes were weighed into the reaction vessel by difference in a dry nitrogen atmosphere box.

12. Methyl lithium

Methyl lithium was obtained from Foote Mineral Company in diethyl ether solution approximately 1.6 M in one mole quantities. When using the reagent, it was syringed in the nitrogen dry-box into a reaction vessel, or syringed from the bottle in the laboratory atmosphere by means of a syringe cap. The solution concentration deteriorates on
standing even under refrigeration and as such must be checked periodically by methanolysis.

13. **Acetic acid**

Concentrated acetic acid was stored in a grease-free vessel over magnesium perchlorate. It was measured at 0° volumetrically.

14. **Solvents**

a. **Tetrahydrofuran**

Reagent grade tetrahydrofuran was dried over lithium aluminum hydride on the vacuum system. The dry material was kept at room temperature in a storage vessel. It was distilled or measured volumetrically into the reaction vessel.

b. **Diethyl ether**

Anhydrous diethyl ether was dried with lithium aluminum hydride on the vacuum system and stored as above. The dry material was distilled into the reaction vessel.

c. **Di-n-butyl ether**

Practical grade di-n-butyl ether was dried with lithium aluminum hydride and then with sodium metal in the form of a sand. The dry material was transferred to a storage bulb and distilled into the reaction vessel as desired in the vacuum system.

d. **Dichloromethane**

Spectroquality dichloromethane was dried with lithium
aluminum hydride in the vacuum system and stored at room temperature. The dry material was distilled into the reaction vessel in the vacuum system.

e. **1,4-Dioxane**

Practical grade 1,4-dioxane was dried with lithium aluminum hydride and then with sodium sand until the sodium no longer became coated. It was stored at room temperature and distilled into the reaction vessel when needed.

f. **Pentane**

Reagent grade pentane was dried over lithium aluminum hydride and stored at room temperature to be distilled into the reaction vessel when needed.

15. **1,2-Bis(tetramethylene)diborane (6)**

The preparation of 1,2-bis(tetramethylene)diborane (6) was achieved in four reactions as described by Young and Shore (33). It was found that the reaction of a 2:1 mole ratio of 1,3-butadiene and diborane (6) in tetrahydrofuran was very difficult to control. The reaction was very vigorous when the temperature was allowed to reach 10°. The reaction could be controlled by cooling the reaction vessel with liquid nitrogen for thirty seconds and then allowing the reaction to warm. Several cycles of warming and cooling were employed, each time only allowing the ice that formed on the reaction vessel to melt.
A more convenient method of preparation of 1,2-bis-(tetramethylene)diborane (6) was employed. Approximately 35 ml of dry di-n-butyl ether was distilled into the reaction vessel containing a Teflon covered magnetic stirring bar and connected to the vacuum system by a vacuum stopcock adapter. A Fisher and Porter Company 90° angle Teflon stopcock was attached to the reaction vessel which had a Fisher and Porter Company 9 mm joint connected to it. A measured amount of 1,3-butadiene was condensed into the reaction vessel at liquid nitrogen temperature. The contents was allowed to warm to room temperature and was then stirred. A -36° slush bath was placed on the vessel. Diborane (6), which was measured in the distillation train, was allowed to come in contact with the solution by opening the stopcock of the adapter. The contents was stirred continuously and the diborane (6) added very smoothly. The pressure was monitored on the "blowout" and when addition became slow, the contents was frozen with liquid nitrogen. The adapter stopcock was closed and the contents was warmed to room temperature with stirring to complete the reaction.

All volatile materials were removed from the reaction mixture at room temperature to leave a viscous, non-volatile polymer. A U-tube was attached to both the reaction vessel and the reservoir, as shown in Figure 2, by means of Fisher and Porter Company 9 mm joints. The apparatus was attached to the vacuum system by means of the stopcock adapter on the
Figure 2. Apparatus for preparation and storage of 1,2-\textit{bis}(tetramethylene)-diborane (6).
reservoir. The U-tube and the reservoir were then evacuated. The polymer was heated to 140° and the volatile products were trapped in the U-tube at -80° by continuous pumping. When it was apparent no more product was collecting, the -80° trap was placed on the U-tube of the reservoir and the desired product was collected in the reservoir by allowing the originally collected product to warm to room temperature. Purification was accomplished by pumping on the product at -10° for 10-15 minutes, with the major impurity being 1,2-tetramethylenediborane (6). The material was found to be 1,2-bis(tetramethylene)diborane (6) by thin film infrared spectroscopy, boron-11 nmr and mass spectrometry.

Approximately 35 millimoles of pure product was isolated when 40 millimoles of diborane (6) and 82 millimoles of 1,3-butadiene were reacted.

16. 1,2-Bis(2,3-dideutero-tetramethylene)-κ-dideuterodiborane (6)

1,2-Bis(2,3-dideutero-tetramethylene)-κ-dideuterodiborane (6) was prepared from 1,3-butadiene and B₂D₆ in a 2:1 mole ratio as described for 1,2-bis(tetramethylene)diborane (6). The pure product exhibited the physical properties of the parent compound. (C₄H₆D₂)₂B₂D₂ was identified by its mass spectrum, which gave a parent mass of 142 as compared to 136 for (C₄H₈)₂B₂H₂. The boron-11 nuclear magnetic resonance spectrum of the deutero compound gave a singlet at
-29.0 ppm which agreed well with the value of -28.5 ppm for 1,2-bis-(tetramethylene)diborane (6). The infrared spectrum indicated approximately 10% H in the bridge position (1612 cm\(^{-1}\)) probably due to scrambling when the polymer was heated.

C. Analytical Procedures

Infrared analysis was used to check the purity of reaction products. Hydridic hydrogen was liberated by acetic acid hydrolysis and measured in the Töpler system. Boron was analyzed by complexation with d-manitol and titration with standard sodium hydroxide.

Reaction stoichiometries were determined by measuring amounts of starting materials and the amounts of excess materials recovered.

D. Amine·\(B_2H_6\) Intermediates

1. Preparation

The amine boranes of ammonia, monomethylamine and trimethylamine were reacted with diborane (6) and each yielded the intermediate amine·\(B_2H_6\). The reactions were carried out in dichloromethane at -78°. Trimethylamine borane was made in the reaction vessel while the other amine boranes were added to the reaction vessel. The apparatus described earlier consisted of a 5 mm nmr sidearm, a Teflon covered magnetic stirring bar, and a rubber stopper. The amine borane was weighed by difference. A measured amount of sol-
vent was condensed into the vessel and the frozen contents was allowed to warm and mix. Next, diborane (6) was condensed at liquid nitrogen temperature into the system in measured increments. The contents was warmed to dry ice temperature between increments allowing sufficient time for complete addition. The pressure was monitored on the "blow-out" by means of a cathetometer. The resulting tensiometric titration gave a break at .5 diborane (6) to 1 amine borane. The titration of ammonia borane with diborane (6) is given in Figure 3.

Diborane (6) could be pumped away from the amine-B₂H₆ systems at -78°. When warmed, the reaction mixtures disassociated into the starting products. The stability of the complex will be discussed in detail later.

2. Boron-11 nuclear magnetic resonance spectra of amine-B₂H₆

The spectra of the intermediates were obtained at -80° to -60°. In all cases only one product was observed in the spectrum. The products were the singly hydrogen-bridged boranes derived from the addition of a BH₃ unit to the amine borane.

Boron-11 nmr spectra of singly hydrogen-bridged boranes are markedly temperature dependent. At about -25° each spectrum consists of a broad singlet, suggesting rapid proton exchange. As the temperature is lowered, fine structure in the spectrum becomes evident, until at -60° seven
Figure 3. Tensiometric titration of \( \text{H}_3\text{BNH}_3 \) with \( \text{B}_2\text{H}_6 \) at \(-78^\circ\text{C}\) in \( \text{CH}_2\text{Cl}_2 \).
lines can be observed. The BH$_3$ group produces a quartet which overlaps a triplet from the BH$_2$ group. The B-H coupling constant for the quartet appears to be significantly smaller than that for the triplet. Figure 4 shows a typical low-temperature spectrum. Table 2 reports chemical shifts and coupling constants observed. Bridge hydrogen is expected to couple with each boron with the B-H-B bond coupling constant being smaller than that for the B-H bond. Thus, each component of the quartet and triplet should be split into a doublet. Such coupling appeared to be present in one sample of methylamine·B$_2$H$_6$ in which each component of the quartet was split into a doublet with a coupling constant of several cycles. In general, however, coupling with bridge hydrogen was not detected (28).

**TABLE 2**

| BORON-11 NUCLEAR MAGNETIC RESONANCE DATA FOR SINGLE HYDROGEN-BRIDGE BORANES AT -65° |
|----------------------------------|---------------|
| $\delta$ (ppm)$^a$             | $J_{(BH_3)}$ (cps)$^b$ |
| NH$_3$·B$_2$H$_6$               | -17.7         | 84            |
| CH$_3$NH$_2$·B$_2$H$_6$         | -18.8         | 89            |
| (CH$_3$)$_3$N·B$_2$H$_6$        | -18.7         | 91            |

$^a$F$_3$B·OEt$_2$ as a reference.

$^b$The coupling constant $J_{(BH_2)}$ is not reported because of difficulty in locating the exact positions of the outer peaks of the triplet.
Figure 4. Boron-ll nuclear magnetic resonance spectrum of CH$_3$NH$_2$B$_2$H$_6$ at -60° in CH$_2$Cl$_2$. 
The preparation of the samples required that the reaction mixture be poured into the sidearm at -78.5° to prevent disassociation of the intermediate. The nmr tube sidearm was sealed off by freezing the contents at liquid nitrogen temperature and using a torch to separate the side-arm from the reaction vessel. Each tube contained a boron trifluoride etherate external standard.

3. Reaction with amines

To each of the aforementioned amine·B₂H₆ intermediates was added one molar equivalent of the corresponding amine. The products from these reactions are given below.

\[
\begin{align*}
H₂B⁻BH₃ + NH₃ & \quad \xrightarrow{-78° \text{ CH₂Cl₂}} \quad BH₂(NH₃)⁺ BH₄⁻ \\
H₂B⁻H⁻BH₃ + NH₂CH₃ & \quad \xrightarrow{-78° \text{ CH₂Cl₂}} \quad BH₂(NH₂CH₃)⁺ BH₄⁻ \\
H₂B⁻H⁻BH₃ + N(CH₃)₃ & \quad \xrightarrow{-78° \text{ CH₂Cl₂}} \quad 2H₃BN(CH₃)₃
\end{align*}
\]

X-ray diffraction data confirmed the formation of BH₂(NH₃)⁺ BH₄⁻ and H₃BN(CH₃)₃, while BH₂(NH₂CH₃)⁺ BH₄⁻ was identified by its boron-11 nmr spectrum (19). The products formed in these reactions are the same products resulting from reaction of diborane (6) with an excess quantity of amine (13,14,15,16,19,25). Thus, so-called "unsymmetrical clea-
vage" products (13,14,15,16) are obtained in the first two reactions while a "symmetrical cleavage" product is observed in the latter case.

The amine reactions with the singly hydrogen-bridged boranes were accomplished by freezing the reaction vessel, which contained the intermediate, to liquid nitrogen temperature and condensing the amine into the system. The reaction vessel is then warmed to -78° and stirred. In the cases where "unsymmetrical cleavage" is expected, the reaction mixture is poured into the nmr sidearm tube and sealed off with a torch. Since the unsymmetrical cleavage products tend to decompose, the spectra were run at about -25° and the identifications were made from the appearance of the quintet due to BH^-4. The x-ray diffraction data was obtained by pumping the solvent off the above reaction mixture and sampling the resultant solid in the dry nitrogen atmosphere box. The data was compared to that obtained from authentic samples of BH_2(NH_3)_2^+ BH^-4 and H_3BN(CH_3)_3.

4. **Boron-10 tracer study**

Boron-10 diborane (6) was added to trimethylamine borane which contained a normal distribution of boron isotopes. The procedure was the same as described for trimethylamine·B_2H_6. After allowing the singly hydrogen-bridged borane to stir at -78°, the diborane (6) was re-
covered by pumping at -78°. The recovered diborane (6) was analyzed by its mass spectrum and the results are described in Table 3. The data clearly indicate that there is essentially no enrichment of boron-11 in the recovered diborane (6).

### Table 3

**Mass Spectra of Recovered Diborane (6)**

<table>
<thead>
<tr>
<th>e/m</th>
<th>B$_2$H$_6$</th>
<th>B$_2$H$_6$</th>
<th>A</th>
<th>B</th>
</tr>
</thead>
<tbody>
<tr>
<td>20</td>
<td>.....</td>
<td>2.5</td>
<td>2.0</td>
<td>2.6</td>
</tr>
<tr>
<td>21</td>
<td>.....</td>
<td>6.4</td>
<td>5.2</td>
<td>6.7</td>
</tr>
<tr>
<td>22</td>
<td>2.6</td>
<td>68.7</td>
<td>62.3</td>
<td>68.5</td>
</tr>
<tr>
<td>23</td>
<td>32.9</td>
<td>29.4</td>
<td>35.1</td>
<td>41.4</td>
</tr>
<tr>
<td>24</td>
<td>88.2</td>
<td>49.0</td>
<td>50.5</td>
<td>54.8</td>
</tr>
<tr>
<td>25</td>
<td>52.6</td>
<td>100</td>
<td>100</td>
<td>100</td>
</tr>
<tr>
<td>26</td>
<td>100</td>
<td>7.4</td>
<td>19.0</td>
<td>15.9</td>
</tr>
<tr>
<td>27</td>
<td>100</td>
<td>2.5</td>
<td>9.7</td>
<td>2.0</td>
</tr>
<tr>
<td>28</td>
<td>.....</td>
<td>.....</td>
<td>.....</td>
<td>.....</td>
</tr>
</tbody>
</table>

---Relative Intensities---

*Relative intensities observed in this study.*

*b* In A, B$_2$$^{10}$H$_6$ was added to (CH$_3$)$_3$NBH$_3$ in CH$_2$Cl$_2$ and the system was continuously stirred for 48 hours at -78° before recovery of diborane (6).

*c* In B, B$_2$$^{10}$H$_6$ was added to (CH$_3$)$_3$NBH$_3$ in glyme and the system continuously stirred for 10 hours at -78° before recovery of diborane (6).
5. Temperature-Concentration Study

As mentioned earlier, the amine-\( B_2H_6 \) intermediates show either a broad singlet or poorly resolved multiplet at -20° and above. Also, the diborane (6), which adds to the amine borane, can be pumped away from the complex. A series of samples were prepared of trimethylamine(borane)\(_2\) and methylamine(borane)\(_2\) in which the amount of diborane (6) was a fraction of that required to form the intermediate. Such a sample was prepared by adding .24 millimoles of diborane (6) to 2.4 millimoles of \((CH_3)_3NBH_3\). This sample was considered a .2 sample, as the amount of diborane (6) added was .2 of that required to make \((CH_3)_3NBH_6\) based on the amount of \((CH_3)_3NBH_3\). The series consisted of .2, .4, .6, .8 and 1.0 samples of both of the intermediates.

The boron-11 nuclear magnetic resonance spectra of the samples were obtained at temperatures ranging from -60° to +27°. The .2 sample gave only the spectrum of the amine borane at all temperatures. The samples which contained higher concentrations of the intermediates exhibited spectra of the intermediates at lower temperature. As the temperature was raised to ambient, the resolution was lost as the signal moved to the position of free diborane (6) in \(CH_2Cl_2\). Also, the spectra of the amine borane at -60° decreased as the sample concentration increased to 1.0. When the temperature was raised and the intermediate disassociated, the amine borane spectra increased in amplitude. Table 4 gives
the data obtained from the series.

TABLE 4
BORON-11 NUCLEAR MAGNETIC RESONANCE DATA OF AMINE-B$_2$H$_6$ AT VARIABLE TEMPERATURE AND CONCENTRATION

<table>
<thead>
<tr>
<th>Amine•B$_2$H$_6$</th>
<th>Temperature</th>
<th>Concentration</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH$_3$NH$_2$•B$_2$H$_6$</td>
<td>.2</td>
<td>.4</td>
</tr>
<tr>
<td>-60°</td>
<td>...</td>
<td>-18.8</td>
</tr>
<tr>
<td>-30°</td>
<td>...</td>
<td>-18.2</td>
</tr>
<tr>
<td>0°</td>
<td>...</td>
<td>-17.7</td>
</tr>
<tr>
<td>+27°</td>
<td>...</td>
<td>-16.9</td>
</tr>
<tr>
<td>(CH$_3$)$_3$N•B$_2$H$_6$</td>
<td>-60°</td>
<td>...</td>
</tr>
<tr>
<td>-30°</td>
<td>...</td>
<td>-18.5</td>
</tr>
<tr>
<td>0°</td>
<td>...</td>
<td>-17.3</td>
</tr>
<tr>
<td>+27°</td>
<td>...</td>
<td>-15.7</td>
</tr>
</tbody>
</table>

The amine borane signal is not reported. All data is in ppm with respect to F$_3$B•OEt$_2$. The chemical shift value of B$_2$H$_6$ is -17.0 ppm at all temperatures in CH$_2$Cl$_2$.

E. 1,2-Bis(tetramethylene) diborane (6) Reaction
Product with Methyl Lithium

1. Preparation

Reaction of 1,2-bis(tetramethylene) diborane (6) was carried out with methyl lithium. The reaction product generated was formulated as a 1:1 reaction which yields a product of empirical composition LiH$_2$B$_2$(C$_4$H$_8$)$_2$CH$_3$. The stoi-
chiometry of this reaction of 1,2-bis(tetramethylene)diborane (6) was determined by reacting a measured amount of organodiborane and methyl lithium and measuring the excess organodiborane recovered.

The reaction product of methyl lithium and 1,2-bis-(tetramethylene)diborane (6) was prepared by three different methods.

In the first reaction a 1:1 mole ratio of methyl lithium and 1,2-bis(tetramethylene)diborane (6) was reacted in diethyl ether at room temperature for several hours. The reaction vessel, described earlier, was weighed before being attached to the organodiborane reservoir. A liquid nitrogen dewar was placed on the reaction vessel and the organodiborane was condensed into the apparatus. After weighing the vessel to determine the amount of 1,2-bis(tetramethylene)diborane (6), a solution of methyl lithium in diethyl ether was syringed into the vessel at -78° in the dry nitrogen atmosphere box. The reaction vessel was connected to the vacuum line, the contents frozen with liquid nitrogen, and the nitrogen evacuated. The contents was allowed to warm to room temperature and stirred for 24 hours. There was no evidence of non-condensible products. All volatile materials were removed from the reaction mixture at room temperature. A viscous, highly solvated material remained in the vessel, which gave off some, but not all, of the solvated ether upon heating. Several attempts were made to remove the solvated ether by extracting
the viscous material with various non-ether solvents, but were unsuccessful.

In a second reaction, methyl lithium was reacted with 1,2-bis(tetramethylene)diborane (6) for 24 hours at 45° with no solvent. Methyl lithium in diethyl ether was syringed into a reaction vessel in the dry nitrogen atmosphere box. The vessel was attached to the vacuum line and evacuated at liquid nitrogen temperature. The contents was warmed and the diethyl ether was removed from the reaction vessel. After weighing the reaction vessel, it was attached to the 1,2-bis(tetramethylene)diborane (6) reservoir and an excess of the organodiborane was condensed onto the methyl lithium at liquid nitrogen temperature. The amount of organodiborane was determined by reweighing the reaction vessel. The contents was placed in a 45° bath and stirred with the excess organodiborane acting as solvent. At the end of the reaction period, the excess 1,2-bis(tetramethylene)diborane (6) was removed and measured. A white micro-crystalline solid remained in the reaction vessel which gave an identical boron-11 nuclear magnetic resonance spectrum to that of the product of the first reaction. When the white solid was dissolved in diethyl ether it behaved like the first reaction product being highly solvated and viscous. An experimental reaction stoichiometry value of .95 1,2-bis(tetramethylene)diborane (6) to 1.00 methyl lithium was obtained from the data.

The procedure in the third reaction was the same as
the first reaction except the solvent employed was di-n-butyl ether. After the methyl lithium was syringed into the reaction vessel, the diethyl ether was removed and replaced by di-n-butyl ether. The material which remained after reaction was very similar to that observed in the first reaction; viscous and highly solvated. The material was found to be identical to the product in the other two reactions.

Related to the first mentioned method was the reaction of methyl lithium and 1,2-bis(2,3-dideutero-tetramethylene)-A-dideuterodiborane (6) in diethyl ether. The procedure was the same as the first method and the product isolated had a similar physical appearance. The boron-11 nuclear magnetic resonance spectrum of Li$D_2B_2(C_4H_6D_2)_2CH_3$ indicated the chemical similarity to Li$H_2B_2(C_4H_8)_2CH_3$.

2. **Properties**

The product of reaction between methyl lithium and 1,2-bis(tetramethylene)diborane (6), Li$H_2B_2(C_4H_8)_2CH_3$, is a white, non-volatile microcrystalline solid at room temperature. It is solvated in ether solvents and is so highly solvated that the solvent can not be removed. The solid and the solvate are stable at room temperature but decompose above 100° with the formation of alkyl substituted borohydrides.

3. **Infrared spectrum of Li$H_2B_2(C_4H_8)_2CH_3**

The infrared spectra of Li$H_2B_2(C_4H_8)_2CH_3$ were ob-
tained from the solvated materials and the white solid mentioned in the three preparative methods. The solvated materials were run as thin films between KBr plates while the solid was run as a nujol mull between salt plates. The spectra obtained from both types of reaction products were identical. The complete infrared spectrum is shown in Figure 5. The absorption bands given in Table 5, represent data from this spectrum.

**TABLE 5**

<table>
<thead>
<tr>
<th>Frequency (cm(^{-1}))</th>
<th>Intensity (a)</th>
<th>Frequency</th>
<th>Intensity (a)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2990</td>
<td>sh</td>
<td>1190</td>
<td>m</td>
</tr>
<tr>
<td>2915</td>
<td>vs</td>
<td>1160</td>
<td>m</td>
</tr>
<tr>
<td>2860</td>
<td>vs</td>
<td>1150</td>
<td>m</td>
</tr>
<tr>
<td>2800</td>
<td>s</td>
<td>1130</td>
<td>m</td>
</tr>
<tr>
<td>2145</td>
<td>s (br)</td>
<td>1100</td>
<td>ms</td>
</tr>
<tr>
<td>1950</td>
<td>m (br)</td>
<td>1065</td>
<td>ms</td>
</tr>
<tr>
<td>1485</td>
<td>w</td>
<td>1030</td>
<td>m</td>
</tr>
<tr>
<td>1450</td>
<td>m</td>
<td>960</td>
<td>m</td>
</tr>
<tr>
<td>1420</td>
<td>w</td>
<td>920</td>
<td>m</td>
</tr>
<tr>
<td>1385</td>
<td>m</td>
<td>840</td>
<td>m</td>
</tr>
<tr>
<td>1310</td>
<td>m</td>
<td>825</td>
<td>m</td>
</tr>
<tr>
<td>1260</td>
<td>sh</td>
<td>795</td>
<td>m</td>
</tr>
</tbody>
</table>

\(a\) Intensities: s=strong; m=medium; w=weak; sh=shoulder br=broad; v=very.
Figure 5. Infrared spectrum of LiH$_2$B$_2$(C$_4$H$_8$)$_2$CH$_3$. 
4. **Boron-11 nuclear magnetic resonance**

spectra of LiH$_2$B$_2$(C$_4$H$_8$)$_2$CH$_3$

Boron-11 nuclear magnetic resonance spectra of LiH$_2$B$_2$(C$_4$H$_8$)$_2$CH$_3$ were obtained for the products from all the methods discussed. An external reference containing boron trifluoride etherate or trimethylborate was inserted into each nmr tube. All spectra consisted of a doublet and a singlet which overlapped the upfield arm of the doublet. The doublet resulted from boron-terminal hydrogen spin coupling, but there was no resolution of the boron-bridge hydrogen spin coupling even at 60°.

The spectrum of LiD$_2$B$_2$(C$_4$H$_6$D$_2$)$_2$CH$_3$ was obtained in the same way as the above parent compound and consisted of two singlets. The presence of deuterium atoms, which do not spin couple with boron nuclei, in place of hydrogen, reduced the doublet in LiH$_2$B$_2$(C$_4$H$_8$)$_2$CH$_3$ to a singlet.

The samples were prepared in a reaction tube equipped with a nmr sidearm tube and a Teflon-coated magnetic stirring bar. Either diethyl or di-n-butyl ether was distilled onto the compound to dissolve it and the solution was poured into the sidearm. The reaction tube and sidearm were frozen and the tube was sealed with a torch.

The boron-11 nuclear magnetic resonance spectra of LiH$_2$B$_2$(C$_4$H$_8$)$_2$CH$_3$ and LiD$_2$B$_2$(C$_4$H$_6$D$_2$)$_2$CH$_3$ are shown in Figure 6. The $J_{BH}$ value for the doublet of LiH$_2$B$_2$(C$_4$H$_8$)$_2$CH$_3$ is 94 cps with a chemical shift value of +15.7 ppm. The sing-
Figure 6. Boron-11 nuclear magnetic resonance spectra of LiH₂B₂(C₄H₈)₂CH₃ and LiD₂B₂(C₄H₆D₂)₂CH₃.
let in the above compound is at +19.2 ppm. For the deuterated compound the chemical shift values of the two singlets at +16.2 ppm and +19.2 ppm. All chemical shift values are with respect to $F_3BOEt_2$.

A comparison of boron-11 nmr data for the above compounds and related compounds is shown in Table 6.

TABLE 6
BORON-11 NUCLEAR MAGNETIC RESONANCE DATA
FOR LiH$_2$B$_2$(C$_4$H$_8$)$_2$CH$_3$ AND RELATED COMPOUNDS

<table>
<thead>
<tr>
<th>Compounds</th>
<th>$\delta$ (ppm)</th>
<th>$J_{BH}$ (cps)</th>
<th>Solvent</th>
</tr>
</thead>
<tbody>
<tr>
<td>LiH$_2$B$_2$(C$_4$H$_8$)$_2$CH$_3$</td>
<td>+15.7</td>
<td>94</td>
<td>Et$_2$O</td>
</tr>
<tr>
<td></td>
<td>+19.2</td>
<td>--</td>
<td></td>
</tr>
<tr>
<td>LiD$_2$B$_2$(C$_4$H$_6$D$_2$)$_2$CH$_3$</td>
<td>+16.2</td>
<td>--</td>
<td>Et$_2$O</td>
</tr>
<tr>
<td></td>
<td>+19.2</td>
<td>--</td>
<td></td>
</tr>
<tr>
<td>NaB$_2$H$_7$</td>
<td>+25.3</td>
<td>102</td>
<td>diglyme</td>
</tr>
<tr>
<td>KB$_3$H$_3$</td>
<td>+12.5</td>
<td>67</td>
<td>THF</td>
</tr>
<tr>
<td>K$_2$H$_2$B$_2$(C$_4$H$_8$)$_3$</td>
<td>+14.5</td>
<td>67</td>
<td>THF</td>
</tr>
</tbody>
</table>

$^a$ $F_3BOEt_2$ reference
$^b$ Bridge-hydrogen coupling unresolved
$^d$ R. Nelson and S. G. Shore, Unpublished results
5. Amine reactions of $\text{LiH}_2\text{B}_2(\text{C}_4\text{H}_8)_2\text{CH}_3$

$\text{LiH}_2\text{B}_2(\text{C}_4\text{H}_8)_2\text{CH}_3$ was reacted with various amine Lewis bases to cleave the hydrogen-bridge system. The products were either symmetrical or unsymmetrical depending on the boron atom to which the amine added.

The reaction of $\text{LiH}_2\text{B}_2(\text{C}_4\text{H}_8)_2\text{CH}_3$ with ammonia was carried out in dichloromethane. $\text{LiH}_2\text{B}_2(\text{C}_4\text{H}_8)_2\text{CH}_3$ was prepared in a reaction vessel equipped with a Fisher and Porter Company Teflon vacuum stopcock adapter and nmr sidearm tube. The preparation was described earlier. After diethyl ether was removed, dichloromethane was distilled onto the compound and the frozen contents was warmed and mixed. Into the solution, ammonia was condensed at liquid nitrogen temperature and the contents was warmed to $-45^\circ$ with stirring. The ammonia was observed to add as the pressure on the blowout decreased with stirring.

\[
\begin{align*}
\text{CH}_3\text{B-H-BH}_2\text{Li}^+ & \xrightarrow{\text{CH}_2\text{Cl}_2\ -45^\circ} \text{NH}_3\text{BCH}_3\text{BH}_2\text{Li}^+
\end{align*}
\]

The cleavage product decomposes at about $-20^\circ$ with the evolution of hydrogen, and extreme care was taken in preparing the nmr tube to insure that none of the material came into contact with glass surfaces warmer than the decomposition.
temperature. The entire reaction vessel with the nmr tube was immersed in a -78° bath before the solution was poured into the sidearm. The contents of the tube was then frozen to liquid nitrogen temperature and the tube was sealed with a torch. The reaction stoichiometry was set at 1:1 amine to LiH₂B₂(C₄H₈)₂CH₃ mole ratio by measuring the ammonia recovered from a reaction involving known amounts of starting material. The excess NH₃ was removed from the completed reaction at -78°, separated from any dichloromethane by fractional distillation, and the ammonia measured as a gas in the calibrated trap system.

The reactions of LiH₂B₂(C₄H₈)₂CH₃ with monomethylamine and dimethylamine were carried out in the same manner as described for ammonia. The only difference was that excess amine was used instead of dichloromethane as a solvent. After methyl lithium and 1,2-bis(tetramethylene) diborane (6) were reacted and the diethyl ether was removed, the amine was added in sufficient quantity to act as both reactant and solvent. The contents was stirred at -78° and was allowed to react for several hours. The products which resulted from these reactions were in each case that of unsymmetrical cleavage. Again, care had to be taken to keep the solution of the cleavage product from coming in contact with glass surfaces above -20°. As in the case of ammonia the products decomposed by hydrogen evolution and the precipitation of a white solid.
The trimethylamine adduct of Li$_2$B$_2$(C$_4$H$_8$)$_2$CH$_3$ was prepared with liquid N(CH$_3$)$_3$ as solvent. The procedure was the same as with the other amines and also the solutions had to be maintained below -20° to prevent decomposition. The method of decomposing was visibly different when compared to the above amines. There was little evidence of hydrogen evolution, but instead, the solution became very viscous and cloudy. The product of symmetrical cleavage was identified. Typical reactions involved approximately 1.0 mmol of Li$_2$B$_2$(C$_4$H$_8$)$_2$CH$_3$ and excess amine to the extent of 0.5 to 1 ml as solvent.

The reaction rates in the case of Li$_2$B$_2$(C$_4$H$_8$)$_2$CH$_3$ with the amine Lewis bases appeared to be fairly slow. When the amine was added to Li$_2$B$_2$(C$_4$H$_8$)$_2$CH$_3$, there was no visible evidence of any change. All of the products had a odor similar to amines. They decomposed rapidly when hydrolyzed and slowly decomposed in air with the evolution of hydrogen.

In the cases where the liquid amines were used as solvents, closed systems capable of withstanding several atmospheres of pressure were employed. Reaction vessels were equipped with Fisher and Porter Company Teflon vacuum stopcocks and 9 mm glass joints. Also, the sealed tubes were capable of withstanding large pressures safely.

All of the reaction products were identified by their boron-11 nuclear magnetic resonance spectra.
6. **Boron-11 nuclear magnetic resonance spectra of amine products**

The reaction products of LiH₂B₂(C₄H₈)₂CH₃ with the amine Lewis bases were identified by their boron-11 nuclear magnetic resonance spectra. As discussed earlier, the products were found to be thermally unstable and the spectra of these products were obtained at temperatures ranging from -45° to -20°. At these temperatures the signal for the anion was the only signal observed. In order to observe the neutral portion of the molecule, the temperature was raised to ambient. At this temperature, there was evidence of some decomposition. The unsymmetrical cleavage products, when the temperature was raised, gave a quartet from decomposition which was at the same position as the unsymmetrical cleavage product from 1,2-tetramethylenediborane (6) and NH₂CH₂ and NH₃ (33). The symmetrical cleavage product did not show this quartet.

The preparation of the sample tubes has been discussed previously. Each tube contained either a trimethylborate or a boron trifluoride etherate external standard, which could be removed from the solution by tipping the tube. Calibration of the spectra was accomplished by using sidebands of a known frequency separation from a standard signal. All chemical shifts are referenced to F₃B·OEt₂ as 0 ppm.

The resolution of the signals was less than in the unsubstituted related compounds. The line broadening was due to increased alkyl substitution.
Table 7 shows the type of cleavage for each reaction and multiplicity of the spectrum. The multiplicity of the spectra arises from spin coupling of the B-H hydrogen ($J=\frac{1}{2}$) with boron.

### TABLE 7

**DESCRIPTION OF THE BORON-11 NUCLEAR MAGNETIC RESONANCE SPECTRA OF AMINE PRODUCTS**

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Type of Cleavage</th>
<th>Multiplicity of Spectrum</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{LiH}_2\text{B}_2(\text{C}_4\text{H}_8)_2\text{CH}_3$</td>
<td>Symmetrical</td>
<td>1:1 doublet for anion; 1:1 doublet for adduct</td>
</tr>
<tr>
<td>$+\text{N}(\text{CH}_3)_3$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$+\text{N}(\text{CH}_3)_2\text{H}$</td>
<td>Unsymmetrical</td>
<td>1:2:1 triplet for anion; singlet for adduct</td>
</tr>
<tr>
<td>$+\text{NCH}_3\text{H}_2$</td>
<td>Unsymmetrical</td>
<td>1:2:1 triplet for anion; singlet for adduct</td>
</tr>
<tr>
<td>$+\text{NH}_3$</td>
<td>Unsymmetrical</td>
<td>1:2:1 triplet for anion; singlet for adduct</td>
</tr>
</tbody>
</table>

The data gathered from the spectra are tabulated in Table 8. Included are data from $\text{B}_2\text{H}_6$, 1,2-tetramethylenedi­borane (6) and 1,2-­bis(tetramethylenediborane (6) inves­tigations.

Typical boron-11 nmr spectra of symmetrical cleavage products and unsymmetrical cleavage products of $\text{LiH}_2\text{B}_2(\text{C}_4\text{H}_8)_2\text{CH}_3$, the products of $\text{N}(\text{CH}_3)_3$ and $(\text{CH}_3)_2\text{NH}$ reactions, respec­
### TABLE 8

**BORON-11 NUCLEAR MAGNETIC RESONANCE DATA**

<table>
<thead>
<tr>
<th>Compound</th>
<th>$\delta$ (ppm)</th>
<th>$J_{BH}$ (cps)</th>
<th>Solvent</th>
</tr>
</thead>
<tbody>
<tr>
<td>$(CH_3)_3NB(CH_3)_3$</td>
<td>+0.1</td>
<td></td>
<td>CH$_3$CN</td>
</tr>
<tr>
<td>$(CH_3)_2NHB(CH_3)_3$</td>
<td>+4.2</td>
<td></td>
<td>CH$_3$CN</td>
</tr>
<tr>
<td>$CH_3NH_2B(CH_3)_3$</td>
<td>+6.8</td>
<td></td>
<td>CH$_3$CN</td>
</tr>
<tr>
<td>$NH_3B(CH_3)_3$</td>
<td>+8.0</td>
<td></td>
<td>CH$_3$CN</td>
</tr>
<tr>
<td>$H_2B_2(C_4H_8)_2$ + $N(CH_3)_3$</td>
<td>-2.0</td>
<td>88</td>
<td>Dioxane</td>
</tr>
<tr>
<td>$+ NH(CH_3)_2$</td>
<td>+1.8</td>
<td>84</td>
<td>NH(CH$_3$)$_2$</td>
</tr>
<tr>
<td>$+ NH_2CH_3$</td>
<td>+5.2</td>
<td>81</td>
<td>NH$_2$CH$_3$</td>
</tr>
<tr>
<td>$+ NH_3$</td>
<td>+13.1</td>
<td>74</td>
<td>CH$_3$CN</td>
</tr>
<tr>
<td>(cation)</td>
<td>+1.6</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Li$H_2B_2(C_4H_8)_2$CH$_3$</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$+ N(CH_3)_3$</td>
<td>+19.1 (anion)</td>
<td>74</td>
<td>N(CH$_3$)$_3$</td>
</tr>
<tr>
<td>$-3.3$</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$+ NH(CH_3)_2$</td>
<td>+20.6 (anion)</td>
<td>76</td>
<td>NH(CH$_3$)$_3$</td>
</tr>
<tr>
<td>$-1.0$</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$+ NH_2CH_3$</td>
<td>+20.6 (anion)</td>
<td>76</td>
<td>NH$_2$CH$_3$</td>
</tr>
<tr>
<td>$+2.8$</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$+ NH_3$</td>
<td>+20.6 (anion)</td>
<td>76</td>
<td>CH$_2$Cl$_2$</td>
</tr>
<tr>
<td></td>
<td>+3.7</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

---

*a* $F_3BOEt_2$ reference  
tively, are shown in Figures 7 & 8. The spectrum of the 
(CH₃)₂NH adduct of LiH₂B₂(C₄H₈)₂CH₃ in Figure 7 is very re-
representative of all the reactions involving unsymmetrical 
cleavage. In each case, the triplet due to the anion appears 
at -40°, but the signal due to the neutral portion of the 
molecule does not appear until about 25°. At 25°, there is 
some decomposition occurring evidenced by the appearance of 
a signal upfield from the triplet. However, if the spectrum 
was recorded quickly, very little decomposition resulted. 
It was noteworthy, that in each case of unsymmetrical cleav-
age, the spectra showed an appreciable amount of starting 
material.

The spectrum of the (CH₃)₃N reaction product of 
LiH₂B₂(C₄H₈)₂CH₃ shown in Figure 8, was obtained in the same 
manner as the unsymmetrical cleavage products. The anion was 
resolved at -30°, while the neutral portion of the molecule 
required ambient temperature to be detected in the spectrum. 
The decomposition of the symmetrical product appeared to be 
more rapid than the other product. This was apparent by the 
decrease in the doublet due to the anion. Also, the doublet 
of the neutral portion of the molecule appeared to have an-
other signal growing in under it.

The relatively good resolution from the anionic 
boron at lower temperatures has been reported previously 
(19,33). The signal due to the neutral boron did require 
temperatures above those for detection of the anionic sig-
Figure 7. Boron-11 nmr spectrum of \((\text{CH})_{32}\text{NH}\) adduct of \(\text{LiH}_2\text{B}(\text{C}_2\text{H}_8)\text{CH}_3\).
Figure 8. Boron-11 nmr spectra of \((\text{CH}_3)_N\) adduct of \(\text{LiH}_2\text{B}(\text{CH}_3)_2\text{CH}_3\) at variable temperature.
nals. This temperature dependence is probably due to nuclear quadrupole spin-lattice relaxation and the line broadening due to alkyl substitution on the boron atom. The combination of these two effects apparently prevents detection of the signal below ambient temperatures. The effect of nuclear quadrupole spin-lattice relaxation resulting in the absence of a detectable signal at lower temperatures has been observed (19,33).
III. RESULTS AND DISCUSSION

A. Diborane (6) intermediates with Lewis bases

1. Preparation

When diborane (6) was added to several amine boranes in methylene chloride, it was found that at -78° an intermediate is formed which has an empirical composition of $\text{LB}_2\text{H}_6$ where L represents the amine. The stoichiometry of the reactions was determined by tensiometric titrations and the break in the curve correspond to .5 diborane (6) to one amine borane. The studies carried out involved ammonia, methylamine and trimethylamine as the bases in the amine boranes. The intermediates were not isolable apecies at room temperature, in fact, care had to be taken in preparing the nmr samples not to allow the solutions to come in contact with surfaces above -78°. Diborane (6) could be pumped away with the amine-$\text{B}_2\text{H}_6$ systems at -78°.

The boron-11 nuclear magnetic resonance spectra of the intermediates were obtained at -60° to -80°. In all cases the only signal observed was that attributed to the intermediate. The spectrum of each intermediate consisted of seven lines at -60° and below. If the intermediate has the singly hydrogen-bridged structure (I), $\text{H}_2\text{B-H-BH}_3^-$

\[ (\text{I}) \]
the boron-11 nmr spectrum would result from a quartet, produced by the BH$_3$ group, which overlaps a triplet due to the BH$_2$ group. Bridging hydrogen is expected to couple with each boron with the B-H-B coupling being smaller than that for a terminal B-H bond. Thus, each component of the quartet and triplet should be split into a doublet. Such coupling, however, with bridge hydrogen was not detected in general. Gaines found no bridge hydrogen coupling in H$_3$B-H-BH$_3$ (28).

The above structure was challenged on the basis of a reinterpretation of the boron-11 nmr spectrum by Eastham (35). The spectrum which appeared in a communication (34) resulted from the ligand being symmetrically attached through a $\pi$ bond between a nonbonding orbital of diborane (6) and the lone pair of the ligand to give (II).

\[
\begin{align*}
\text{H}_2\text{B} & \quad \text{H} \\
\text{H} & \quad \text{BH}_2 \\
\text{L} &
\end{align*}
\]

(II)

In order to determine which structure was correct, experimental work was carried out using $^{10}\text{B}_2\text{H}_6$. To (CH$_3$)$_3$NBH$_3$, which contained a normal distribution of boron isotopes, was added $^{10}\text{B}_2\text{H}_6$. In principle, this gave rise to one of two structures:
Since the diborane (6) can be recovered by pumping, the recovered diborane (6) was analyzed mass spectrometrically. From the data presented in Table 3, it can readily be seen that there is essentially no enrichment of boron-11 in the recovered diborane (6). This result is consistent with structure (I) and refutes the presence of structure (II). For structure (II), the symmetrical attachment of the amine to diborane (6) requires that a statistical distribution of boron isotopes be present in the recovered diborane (6).

Thermodynamic data also speak against structure (II). The heat of formation of \((\text{CH}_3)_3\text{NBH}_3\) in solution from diborane (6) and trimethylamine is about -22 kcal/mole (42). From a thermodynamic cycle it can be seen that for structure (II) to be formed, the heat of formation of structure (II) would have to exceed that of \((\text{CH}_3)_3\text{NBH}_3\). It is doubtful that such an amount of energy is available from interaction of a vacant nonbonding orbital with an electron donor.

The principal argument upon which structure (II) is based rests in the claim that the boron-11 nmr spectrum
assigned to structure (I) is virtually superimposable on the first boron-11 nmr spectrum published 15 years ago by Ogg (43). It should be recognized, however, that Ogg's spectrum was taken at 6 Mc while the spectra obtained herein were run at 19.25 Mc. The diborane (6) spectrum in methylene chloride at 19.25 Mc, shown in Figure 9, consists of nine well-resolved lines, a triplet of triplets, in contrast to the relatively poor resolved septet assigned to structure (I).

The $\text{B}_2\text{H}_6^{10}$ study and the thermodynamic data available point to structure (I) as being more consistent.

In an attempt to understand or detect any exchange process which might have been operative in the system, a study was undertaken in which both the temperature and the concentration of the intermediate, with respect to the amount of amine borane, were varied. The results of the study were reported in Table 4. The data obtained were nearly identical for $(\text{CH}_3)_3\text{N} \cdot \text{B}_2\text{H}_6$ and $\text{CH}_3\text{NH}_2 \cdot \text{B}_2\text{H}_6$ under the conditions studied. As the temperature was taken from $-60^\circ$ to $+27^\circ$, in every case the signal gradually shifted to the value obtained for diborane (6) in methylene chloride. Also, by varying the concentration of the intermediate, the boron-11 signal of the intermediate varied directly as compared to the signal of the amine borane. Thus, at higher concentrations of the intermediate, its boron-11 nmr signal was of a greater amplitude than that of the amine borane, while at lower concentration the reverse was true.
Figure 9. Boron-11 nmr spectrum of $\text{B}_2\text{H}_6$ at 19.25 Mc.
From this study, it is clear that there is an interaction at low temperature since the signal in the boron-11 nmr spectra shifts to the value of free diborane (6) in methylene chloride at room temperature. The resolution of the diborane (6) spectra alone in methylene chloride remains intact over the temperature range of -60° to +27°. The study appears to reflect the information obtained from the tensiometric titration but does not rule out the possibility of an interaction between the intermediates and any diborane (6) dissolved in the solvent.

2. Reactions with amine

Addition of one mole of amine per mole of singly hydrogen-bridged species gave the products cited in the equation below. X-ray powder diffraction data confirmed the formation of $\text{H}_2\text{B(NH}_3\text{)}_2^+ \text{BH}_4^-$ and $(\text{CH}_3)_3\text{NBH}_3$ while $\text{H}_2\text{B(NH}_2\text{-CH}_3\text{)}_2^+ \text{BH}_4^-$ was identified by its boron-11 nmr spectrum (19). The products formed in these reactions are the same as those resulting from the reaction of diborane (6) with excess amine (13,14,15,16,19,25). Thus, so-called unsymmetrical cleavage products are obtained in the first two reactions while a symmetrical cleavage product is observed in the latter case.

$$\text{H}_2\text{B-H-BH}_3 + \text{NH}_3 \rightarrow \text{NH}_3 \xrightarrow{-78^\circ} \text{CH}_2\text{Cl}_2 \rightarrow \text{H}_2\text{B(NH}_3\text{)}_2^+ \text{BH}_4^-$$
In view of the results presented, the tensiometric titration, the tracer study, the concentration-temperature dependence study and the amine reactions; it is not unreasonable to suppose that diborane (6) reacts with a ligand in a stepwise fashion. The first step involves the displacement of one hydrogen from the bridge position.

\[
\begin{align*}
H_2B-H-BH_3 + NH_2CH_3 & \xrightarrow{-78^\circ} H_2B(NH_2CH_3)_2^+ BH_4^- \\
\text{NH}_2\text{CH}_3 & \\
Heat & \\
CH_2Cl_2 & \\
H_2B-H-BH_3 + N(CH_3)_3 & \xrightarrow{-78^\circ} 2H_3BN(CH_3)_3 \\
\text{N(CH}_3)_3 & \\
\text{Heat} & \\
CH_2Cl_2 & 
\end{align*}
\]

The second step, involving displacement of hydrogen from the remaining bridge, would determine the type of product generated.

\[
\begin{align*}
H_2B\overset{\text{H}}{\text{BH}}_2 + L & \xrightarrow{} H_2B-H-BH_3 \\
\overset{\text{L}}{} & \\
& \\
H_2B-H-BH_3 + L & \rightarrow H_2BL_2^+ BH_4^- \text{ unsymmetrical cleavage} \\
\overset{\text{L}}{} & \\
& \\
H_2B-H-BH_3 + L & \rightarrow 2LBH_3 \text{ symmetrical cleavage} \\
\overset{\text{L}}{} & 
\end{align*}
\]

This scheme is consistent with the observation that with increasing steric bulk of methyl-substituted amine, the yield of symmetrical cleavage product increases (4,15,19).
The suggestion (25) that reactions of diborane (6) with Lewis bases at low temperature can involve unsymmetrical cleavage, although the product can rearrange to a symmetrical product at a particular temperature, does not coincide with experimental data. No evidence for facile rearrangement was detected between $\text{H}_3\text{NBH}_3$ and $\text{H}_2\text{B(NH}_3)_2\text{BH}_4^-$ in liquid ammonia (16, 17, 26, 27). Also, the only observed product at temperature from -60° to ambient in the reaction of $(\text{CH}_3)_3\text{NBH}_3$ with $(\text{CH}_3)_2\text{N}$ was the symmetrical product $(\text{CH}_3)_2\text{NBH}_3$.

Although the data presented above does not account for all the factors operating in the reaction of diborane (6), it does allow for a reasonable explanation of the path by which the molecule reacts with Lewis bases. The steric requirements of diborane (6) are reflected in the methyl-substituted amine series, but electronic factors which certainly play a large part in the determination of the type of cleavage product are less than fully understood.

B. 1,2-Bis(tetramethylene)diborane (6)

1. Preparation

The methods for preparing 1,2-bis(tetramethylene)-diborane (6) were discussed by Young and Shore (33). It was found that the most successful preparation involving diborane (6) and 1,3-butadiene in tetrahydrofuran was also the most dangerous. Since considerable quantities of the
organodiborane were required, a safer reaction was devised which allowed for larger scale preparations.

A 2:1 mole ratio of butadiene and diborane (6) was reacted by addition of diborane (6), as a gas, to a solution of butadiene in di-n-butyl ether. The reaction was carried out at -35°. The expected polymeric organoborane was formed. Upon heating, the material to 120°, a clear, colorless liquid was liberated. The material was identified by comparing its physical properties to those determined by previous workers (31,33).

This preparation has the advantage of allowing the synthesis of a large amount of 1,2-bis(tetramethylene)diborane (6) by a safe means. The separation was easy and clean, and the product required very little purification. The yields from this preparation were better than 80%.

2. Bridge cleavage reactions

a. Preparation of LiH<sub>2</sub>B<sub>2</sub>(C<sub>4</sub>H<sub>8</sub>)<sub>2</sub>CH<sub>3</sub>

The synthesis of LiH<sub>2</sub>B<sub>2</sub>(C<sub>4</sub>H<sub>8</sub>)<sub>2</sub>CH<sub>3</sub> was carried out in three reactions employing different conditions.

A 1:1 mole ratio of methyl lithium and 1,2-bis(tetramethylene)diborane (6) were reacted in diethyl ether at room temperature for several hours. The product generated was a highly solvated viscous liquid. A second reaction was carried out in the absence of solvent by heating methyl lithium in excess 1,2-bis(tetramethylene)diborane (6) to 45° for 24
hours. The product, when the excess organoborane was removed, was a white solid. A reaction stoichiometry of .95 \textit{1,2-bis} \textit{(tetramethylene)}diborane (6) to 1.00 methyl lithium was obtained from the reaction. When diethyl ether was added to the solid, it behaved like the first reaction product. Both materials were quite viscous and released the solvated diethyl ether upon gentle heating. Increased heating caused decomposition of the reaction product. The materials exhibited identical infrared spectra with broad resonances centered at 2145 cm\(^{-1}\) and 1950 cm\(^{-1}\). The boron-11 nuclear magnetic resonance spectra of each product showed a doublet and a singlet which overlapped the upfield arm of the doublet. The doublet, centered at +15.7 ppm, had a coupling constant of 94 cps while the singlet showed a chemical shift value of +19.2 ppm with respect to \(\text{F}_3\text{B} \cdot \text{OEt}_2\). Bridge hydrogen spin coupling was not observed.

\(\text{LiH}_2\text{B}_2\text{(C}_4\text{H}_8\text{)}_2\text{CH}_3\) was also prepared in a third reaction involving a 1:1 mole ratio of methyl lithium and \textit{1,2-bis} \textit{(tetramethylene)}diborane (6) in di-n-butyl ether. The product again was viscous and highly solvated by the bulkier ether.

In a reaction employing the same conditions as the first reaction, methyl lithium was reacted with \textit{1,2-bis-} (2,3-dideutero-tetramethylene)-\(\mu\)-dideuterodiborane (6) in diethyl ether. The reaction product was identical to the
products isolated in the above reaction in its appearance. The boron-11 nuclear magnetic resonance spectrum of a diethyl ether solution of the deuterated material showed two singlets at chemical shift values of +16.5 ppm and +19.5 ppm with respect to $\text{F}_3\text{B} \cdot \text{OEt}_2$.

The stoichiometry of the methyl lithium reaction with 1,2-bis(tetramethylene)diborane (6) when combined with the boron-11 nmr data led to the formulation of a structure for $\text{LiH}_2\text{B}_2(\text{C}_4\text{H}_8)_2\text{CH}_3$ which is shown in Figure 10. Since $\text{CH}_3$ is electronically analogous to $\text{NH}_3$, the compound can be considered the analog of the intermediate in step (I), in the ammonia reaction of 1,2-bis(tetramethylene)diborane (6).

![Diagram](image)

Although this intermediate has not been isolated, its formation seems very probable in view of the results presented earlier on the diborane reactions with amines. $\text{LiH}_2\text{B}_2(\text{C}_4\text{H}_8)_2\text{CH}_3$ represents, by analogy, the intermediate in the bridge cleavage reaction of 1,2-bis(tetramethylene)-diborane (6) with amine Lewis bases.
Figure 10. Proposed structure of LiH$_2$B$_2$(C$_4$H$_8$)$_2$CH$_3$. 
The proposed structure was formulated on the data presented. The 1:1 molar ratio in which the reactants combined and the absence of methane evolved gave the molecularity of the product. The boron-11 nuclear magnetic resonance data of LiH$_2$B$_2$(C$_4$H$_8$)$_2$CH$_3$ and its partially deuterated analog, LiD$_2$B$_2$(C$_4$H$_6$D$_2$)$_2$CH$_3$, yielded information concerning the nature of the hydrogen atoms attached to the boron atoms. The spectra are presented in Figure 6.

The infrared spectrum of LiH$_2$B$_2$(C$_4$H$_8$)$_2$CH$_3$, shown in Figure 5, exhibited broad resonances at 2145 and 1950 cm$^{-1}$ in the region of the spectrum usually attributed to boron-hydrogen terminal stretching. Taylor and Matsui have reported that in the related systems, B$_2$H$_7^-$, B$_2$(CH$_3$)$_6$H$_7^-$ and B$_2$(C$_2$H$_5$)$_6$H$^-$, broad bands of moderate intensity were observed at 2050, 2100 and 1915 cm$^{-1}$, respectively (44). There has been very little work done, however, concerning the spectral properties of trialkylborohydrides. The few compounds that have been prepared (45,46,47) contain peaks in the range 1800-2000 cm$^{-1}$. Since the systems studied by Taylor and Matsui could possibly be starting material, trialkylborohydrides, or in the case of B$_2$H$_7^-$, the terminal boron-hydrogen stretching frequency, this particular area deserves additional studies to clarify the uncertainties. Until such time, the contention that bands in a certain region of the infrared range correspond to a particular stretching frequency (B-H-B or B-H), can no longer be a definite
b. Amine reactions of \( \text{LiH}_2\text{B}_2(\text{C}_4\text{H}_8)_2\text{CH}_3 \)

\( \text{LiH}_2\text{B}_2(\text{C}_4\text{H}_8)_2\text{CH}_3 \) was found to react with ammonia and the methyl-substituted amines. It was cleaved unsymmetrically not only by \( \text{NH}_3 \), but also by \( \text{NH}_2\text{CH}_3 \) and \( \text{NH} (\text{CH}_3)_2 \). This fact may seem somewhat surprising when compared to similar reactions of \( \text{B}_2\text{H}_6 \), 1,2-tetramethylenediborane (6) and 1,2-\text{bis} (tetramethylene)diborane (6).

Methylene chloride or excess amine were found to be better solvents than ether in these reactions.

Reaction of \( \text{LiH}_2\text{B}_2(\text{C}_4\text{H}_8)_2\text{CH}_3 \) with ammonia, methylamine and dimethylamine produced the unsymmetrical cleavage product. As mentioned earlier, if \( \text{LiH}_2\text{B}_2(\text{C}_4\text{H}_8)_2\text{CH}_3 \) is considered the analog in the stepwise attack of ammonia with 1,2-\text{bis} (tetramethylene)diborane (6), then these amines attack the boron to which the \( \text{CH}_3 \) group is already attached.

\[
\begin{array}{c}
\text{L + } H - B - B - \text{CH}_3 \text{ Li}^+ \rightarrow H_2B - \text{CH}_3BL \text{ Li}^+ \\
\text{L}=\text{NH}_3, \text{NH}_2\text{CH}_3, \text{NH} (\text{CH}_3)_2 \\
\end{array}
\]

These unsymmetrical cleavage products were found to decompose slowly, over a period of 24 hours, at temperatures above approximately \(-20^\circ\). Decomposition was evident by the evolu-
tion of hydrogen and the formation of a white solid in the reaction vessel.

In the reaction of trimethylamine with \( \text{LiH}_2\text{B}_2(\text{C}_4\text{H}_8)_2^- \), the resulting product was that involving symmetrical cleavage of the single hydrogen bridge. In this case, the Lewis base attached itself to the boron atom not having the \( \text{CH}_3^- \) group.

\[
\begin{align*}
\text{L} + \text{H-B-H-B-CH}_3 \text{Li}^+ &\rightarrow \text{LBH CH}_3\text{BH Li}^+ \\
\text{L} = \text{N(CH}_3)_3 &\quad \text{symmetrical cleavage}
\end{align*}
\]

The product from this reaction was also unstable. When warmed above -20°, it decomposed in about 12 hours, evidenced by the formation of a white solid and coagulation of the reaction solution to a jelly-like substance. There was only a small amount of hydrogen evolution.

The products of the bridge cleavage reactions identified by their boron-11 nmr spectra are shown in Table 9.

The boron-11 nuclear magnetic resonance spectra were obtained over a temperature range of -60° to ambient temperature. The samples were allowed to warm above the decomposition point in order to observe the entire spectrum. The spectra of the unsymmetrical cleavage products consisted,
### TABLE 9

**BORON-11 NUCLEAR MAGNETIC RESONANCE DATA FROM AMINE REACTIONS**

<table>
<thead>
<tr>
<th>Compound</th>
<th>$\delta^a$ (ppm)</th>
<th>$J_{BH}$ (cps)</th>
<th>Multiplicity of Spectrum</th>
<th>Solvent</th>
</tr>
</thead>
<tbody>
<tr>
<td>(CH$_3$)$_3$N adduct</td>
<td>+19.1</td>
<td>74</td>
<td>1:1 doublet</td>
<td>(CH$_3$)$_3$N</td>
</tr>
<tr>
<td>of LiH$_2$B$_2$(C$_4$H$_8$)$_2$CH$_3$</td>
<td>-3.3</td>
<td></td>
<td>1:1 doublet</td>
<td></td>
</tr>
<tr>
<td>(CH$_3$)$_2$NH adduct</td>
<td>+20.6</td>
<td>76</td>
<td>1:2:1 triplet</td>
<td>(CH$_3$)$_2$NH</td>
</tr>
<tr>
<td>of LiH$_2$B$_2$(C$_4$H$_8$)$_2$CH$_3$</td>
<td>-1.0</td>
<td></td>
<td>singlet</td>
<td></td>
</tr>
<tr>
<td>CH$_3$NH$_2$ adduct</td>
<td>+20.6</td>
<td>76</td>
<td>1:2:1 triplet</td>
<td>CH$_3$NH$_2$</td>
</tr>
<tr>
<td>of LiH$_2$B$_2$(C$_4$H$_8$)$_2$CH$_3$</td>
<td>+2.8</td>
<td></td>
<td>singlet</td>
<td></td>
</tr>
<tr>
<td>NH$_3$ adduct</td>
<td>+20.6</td>
<td>76</td>
<td>1:2:1 triplet</td>
<td>CH$_2$Cl$_2$</td>
</tr>
<tr>
<td>of LiH$_2$B$_2$(C$_4$H$_8$)$_2$CH$_3$</td>
<td>+3.7</td>
<td></td>
<td>singlet</td>
<td></td>
</tr>
</tbody>
</table>

---

$a$ F$_3$B·OEt$_2$ as reference

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in each case, of a 1:2:1 triplet and a singlet. The triplet resulted from spin coupling of hydrogen with the boron atom in the anionic portion of the molecule. It was necessary to raise the temperature to obtain a good boron-11 nmr signal of the neutral portion of the molecule.

The spectrum of the symmetrical cleavage product consisted of two doublets. The high field doublet was assigned to the anionic portion of the symmetrical cleavage product. In order to observe the adduct portion of the molecule, the temperature of the sample was raised to +25°.

The reactivity of LiH₂B₂(C₄H₈)₂CH₃ appeared to be considerably lower than that of the parent organodiborane toward amine Lewis bases. It is evident from the boron-11 nmr spectra obtained that when LiH₂B₂(C₄H₈)₂CH₃ was reacted with an amine Lewis base, the reaction did not go to completion. Even when large excesses of amine were used, there remained an appreciable amount of what was apparently the starting material. This situation held for both the symmetrical and unsymmetrical reactions. This situation was not anticipated, but if one considers the large difference in basicity between CH₃⁻ and NH₃, it is reasonable to suspect that LiH₂B₂(C₄H₈)₂CH₃ is a weaker Lewis acid toward amines than the intermediate in stepwise reaction of 1,2-bis(tetramethylene)diborane (6) with ammonia.
From the spectra obtained, there appeared to be only one type cleavage product generated in the reactions. By comparing the cleavage products obtained in the reactions of 1,2-bis(tetramethylene)diborane (6) and LiH₂B₂(C₄H₈)₂CH₃ with amine bases, there was an apparent consistency between the type of cleavage product and the steric factors of the reacting molecules. The data from the two studies are presented in Table 10.

The chemical shifts for the compounds in Table 9 exhibit a familiar trend. Heitsch (48) reports that chemical shifts for the adducts of B(CH₃)₃, as reported in Table 8, increase according to the following sequence:

\[ \text{NH}_3 > \text{NH}_2\text{CH}_3 > \text{NH(CH}_3)_2 > \text{N(CH}_3)_3 \]

The portion of the molecule, to which the amine has added in the unsymmetrical cleavage reactions of LiH₂B₂(C₄H₈)₂CH₃, shows the same trend in chemical shift.

The factors which determine the type of cleavage product formed when a Lewis base reacts with a hydrogen bridge system are not clearly understood, but there is considerable evidence to show that steric factors are very im-
<table>
<thead>
<tr>
<th>Reactants</th>
<th>Unsymmetrical Cleavage Product</th>
<th>Symmetrical Cleavage Product</th>
</tr>
</thead>
<tbody>
<tr>
<td>H₂B₂(C₂H₄)₂ + NH₃</td>
<td>(NH₃)₂B⁺·BH₂</td>
<td>No evidence for product</td>
</tr>
<tr>
<td>+NH₂CH₃</td>
<td>No evidence for product</td>
<td>CH₃NH₂BH HBNH₂CH₃</td>
</tr>
<tr>
<td>+NH(CH₃)₂</td>
<td>No evidence for product</td>
<td>(CH₃)₂NBH HBNH(CH₃)₂</td>
</tr>
<tr>
<td>+N(CH₃)₃</td>
<td>No evidence for product</td>
<td>(CH₃)₃NBH HBN(CH₃)₃</td>
</tr>
<tr>
<td>Reactants</td>
<td>Unsymmetrical Cleavage Product</td>
<td>Symmetrical Cleavage Product</td>
</tr>
<tr>
<td>-------------------------------</td>
<td>--------------------------------</td>
<td>-----------------------------</td>
</tr>
<tr>
<td>LiH₂B₂(C₄H₈)₂CH₃ + NH₃</td>
<td><img src="" alt="Diagram" /></td>
<td>No evidence for product</td>
</tr>
<tr>
<td>+NH₂CH₃</td>
<td><img src="" alt="Diagram" /></td>
<td>No evidence for product</td>
</tr>
<tr>
<td>+NH(CH₃)₂</td>
<td><img src="" alt="Diagram" /></td>
<td>No evidence for product</td>
</tr>
<tr>
<td>+N(CH₃)₃</td>
<td><img src="" alt="Diagram" /></td>
<td>No evidence for product</td>
</tr>
</tbody>
</table>
portant. The tendency to produce unsymmetrical cleavage in the diborane compounds diminishes with increased alkyl substitution on both the amine and the diborane. While diborane is cleaved totally in a symmetric fashion by \((\text{CH}_3)_3\text{N}\), 1,2-tetramethylenediborane (6) and 1,2-\textit{bis}(tetramethylene)-diborane (6) are cleaved symmetrically by less hindered bases \((\text{CH}_3)_2\text{NH}\) and \(\text{CH}_3\text{NH}_2\), respectively.

It appears that this study extends the previous evidence involving the importance of steric factors. However, the results may also yield some information regarding electronic factors. It was not surprising when ammonia and methylamine cleaved the single hydrogen-bridge anion unsymmetrically. The unsymmetrical cleavage by dimethylamine was unexpected. The anion, as mentioned previously, is electronically analogous to the postulated intermediate in the stepwise reaction of 1,2-\textit{bis}(tetramethylene)diborane (6) with ammonia. By analogy to the 1,2-\textit{bis}(tetramethylene)-diborane (6) reactions, it might have been expected that the dimethylamine reaction would be symmetrical, considering only steric factors. Caution must be exercised, however, in extending the analogy of the \(\text{CH}_3^-\) anion to ammonia. Although the two species are electronically analogous, there is certainly a marked difference in their sizes. It could be that the reaction of dimethylamine with the anion may be controlled more by the relative difference between \(\text{CH}_3^-\) and \(\text{NH}_3\) than by their similarities.
The only evidence for the cleavage products being totally one type was their boron-11 nmr spectra. The results, when considered with the data obtained from the organodiborane reactions studied by Young and Shore (33), can be explained by the slower reaction rate that accompanies increased alkyl substitution on diborane. It is possible that in the slower reactions, the type of cleavage product is controlled by thermodynamic and not kinetic effects. This would account for the absence of a symmetrical product in the (CH$_3$)$_2$NH reaction of LiH$_2$B$_2$(C$_4$H$_8$)$_2$CH$_3$ when such a product might be expected.
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42. A. C. Boyd, Jr., Dissertation Abstr., 17, 1908 (1957).